

Spectroscopic study of CN_x films grown by magnetron sputter deposition

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INTRODUCTION

The determination of the chemistry and microscopic structure of carbon nitride films is of considerable interest because of the scientific and technological importance of such materials [1-4]. CN_x films typically exhibit interesting properties such as fullerene-like or amorphous microstructures, high hardness and extremely elastic properties [2,3], and a good tribological performance [4]. As a consequence of their properties, such films may have found applications as protective coating as well as lubricants.

Several experimental techniques including Fourier transform infrared spectroscopy (FTIR), x-ray photoemission spectroscopy (XPS), and high-resolution electron microscopy (HREM) have been used to investigate the microscopic bonding and structure in CN_x films. Despite all these efforts, the correlation between microstructure and microscopic bonding is far from being understood. Because of their local character the near edge x-ray absorption fine structure (NEXAFS) and x-ray emission spectroscopy (XES) techniques are well suited for structural studies of disordered systems and they have been extensively applied to study materials such as a-C films [5], diamond and graphite [6-9]

EXPERIMENT

Deposition of carbon nitride thin films were carried out in a dc magnetron sputtering with a base pressure of 1×10^{-5} pa. The target was a high purity of 99.99% pyrolytic graphite disc, separated by 10 Cm from the resistively heated substrate holder. The target was sputter clean prior to each deposition, with a shutter shielding the substrate from the depositing species. The substrates were Si(001) wafers. They were first cleaned ultrasonically in acetone and alcohol baths consecutively, and heated under vacuum in the deposition system up to 850  C for 10 minutes to remove the surface oxide prior to setting the desired substrate temperature. 99.9999% pure nitrogen was introduced into the sputtering chamber through a mass flow controlling until the required N₂ pressure was obtained. In this experiment we have measured three CN_x samples which were made at different substrate temperatures (T_s).

The experiments were performed at beamline 7.0 at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory. The beamline comprises a 99-pole, 5 cm period undulator and a spherical-grating monochromator [10]. NEXAFS spectra were obtained by measuring the total electron yield from the sample. The resolution of the monochromator was set to 0.15 and 0.3 eV, respectively, for C and N *1s* absorption edge. The NEXAFS spectra were normalized to the incident photon current using a clean gold mesh to correct for intensity fluctuation of the photon beam. The XES spectra were recorded using a high-resolution grazing-incidence x-ray fluorescence spectrometer [11]. During the XES measurement, the resolution of the beamline was the same as that in XAS measurement, and the resolution of the fluorescence spectrometer was set to 0.45 eV and 0.65 eV, respectively, for C and N *K* emission.

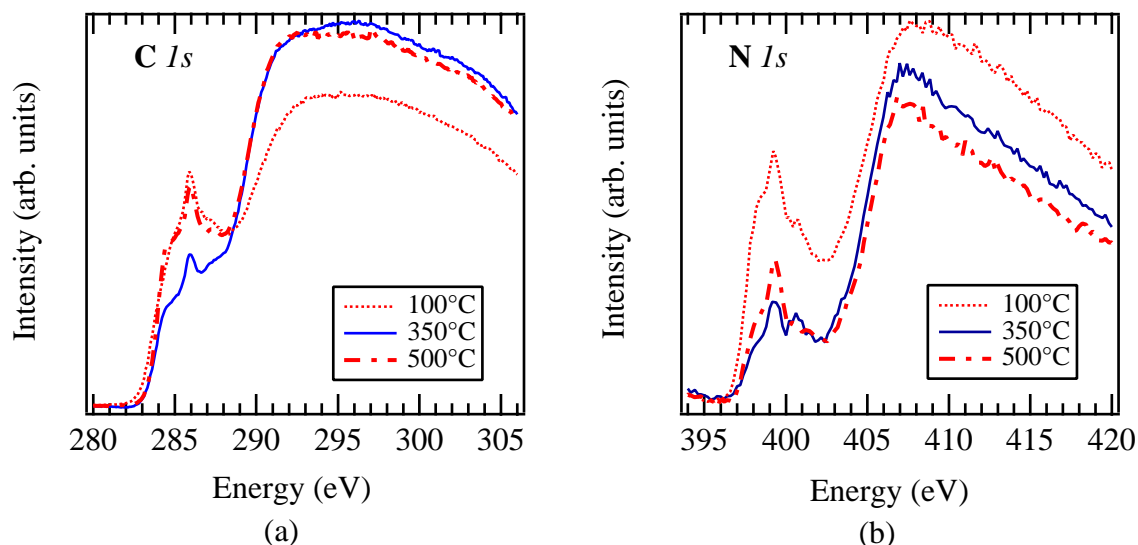


Figure 1. X-ray absorption spectra from CN_x thin films at C $1s$ threshold (a) and N $1s$ threshold (b).

RESULTS

The NEXAFS measurement at C $1s$ and N $1s$ edge from different temperature made CN_x films are presented in Figure 1. The near-edge x-ray absorption occurs when core electrons are excited to unoccupied states. The low energy region (284 - 288 eV) of the C $1s$ spectra is composed of a π^* (C = N) transition at 286 eV, with a low-energy shoulder at 285 eV (π^* , C = C). The very broad σ^* resonance centered around 296 eV corresponds to C-C, C-N, C = C, and C = N bonds (sp^2 and sp^3 character) and reveals the disordered nature of the film.

The N $1s$ spectra show the π^* (N = C) transition at 398.3 eV. The absorption profile in the π^* resonance region is similar to C $1s$ spectra. The σ^* resonance is sharpening in N $1s$ spectra reflects less bonds to nitrogen sites. There is a shift between the σ^* resonance of different CN_x films, from about 407.7 eV of 100°C sample to 407 eV of 500°C sample.

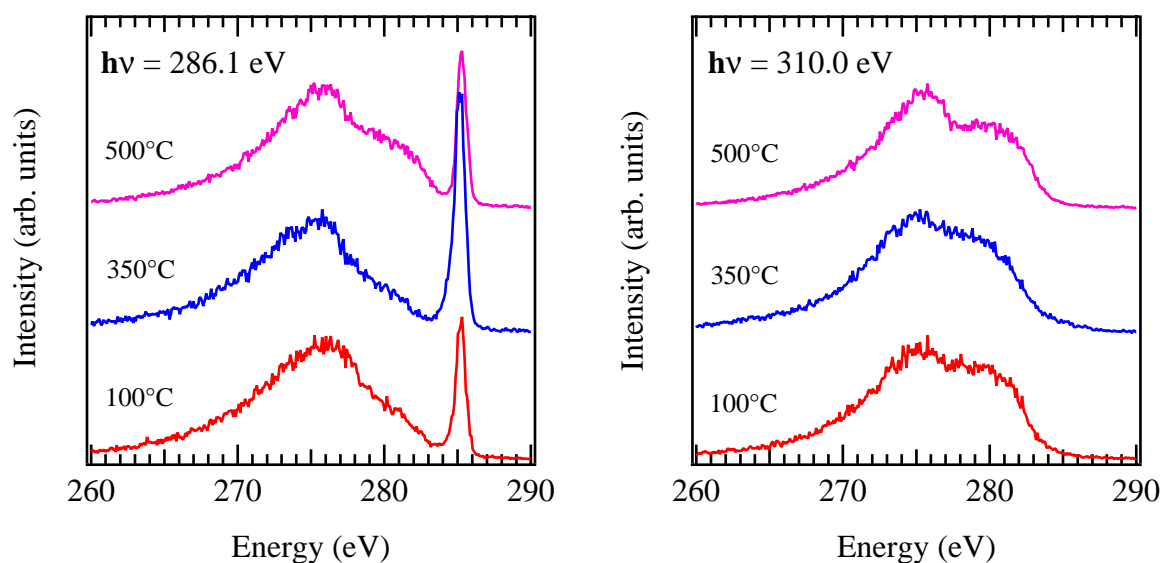


Figure 2. C K x-ray emission spectra with resonant excitation (left) and non-resonant excitation (right).

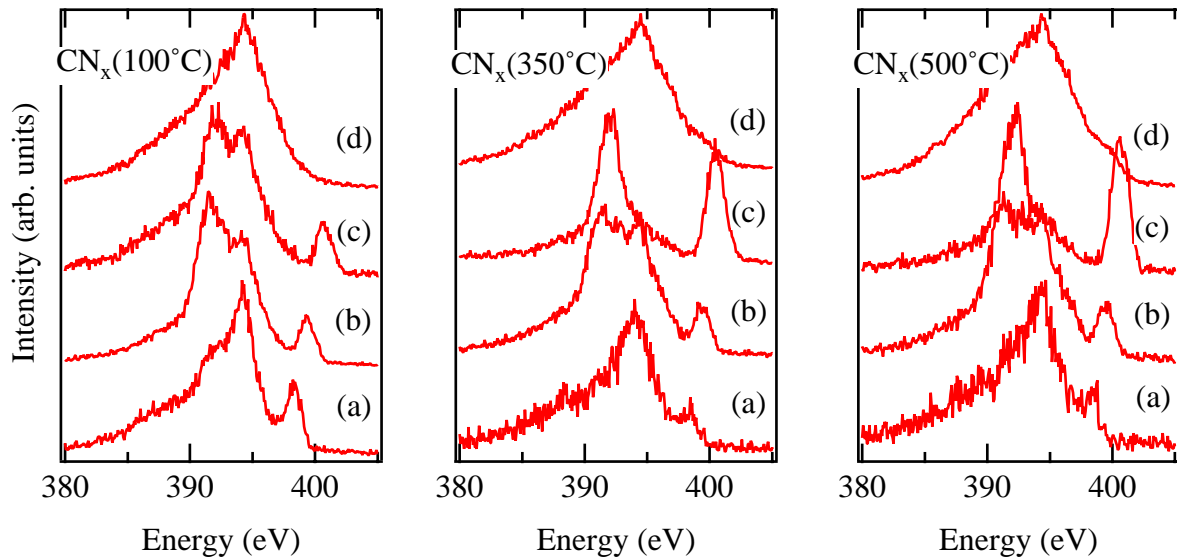


Figure 3. N K x-ray emission spectra with the excitation energy of 398.3 eV (a), 399.3 eV (b), 400.6 eV (c), and 407.9 eV (d).

The C K emission spectra of different T_s samples are presented in Figure 2. The C emission bands are centered around 276 eV, no significant difference was observed as a function of T_s .

The N K emission spectra of different T_s samples are presented in Figure 3. The spectral profile shows a strong dependence upon the incoming photon energy. For the high photon energy excitation (Top curves), the N emission bands are centered around 394.5 eV, besides the total valence band-width increases with T_s , no significant difference was observed as a function of T_s . The great difference upon T_s is observed at the 400.6-eV-excited resonant x-ray emission spectra.

DISCUSSION

The resonant N K emission spectra (curves a, b, and c in Figure 3) can be deconvoluted to two peak structures. The fact that the N resonant x-ray emission spectra show two relatively large peaks at 392 and 394 eV, is due to two different N bonding configurations in the films. Based on the structural analyses, two N configurations are expected, one with N located in the hexagonal C planes and one corresponding to a position in which the bonding configuration is more tetrahedral-like. The latter can be the case if N atoms occupy positions where a basal plane in a basal structure unit terminates. We can assign the N peak at 392 eV to be due to N bonded to sp^3 -hybridized C and that at 394 eV to N bonded to sp^2 -hybridized C.

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